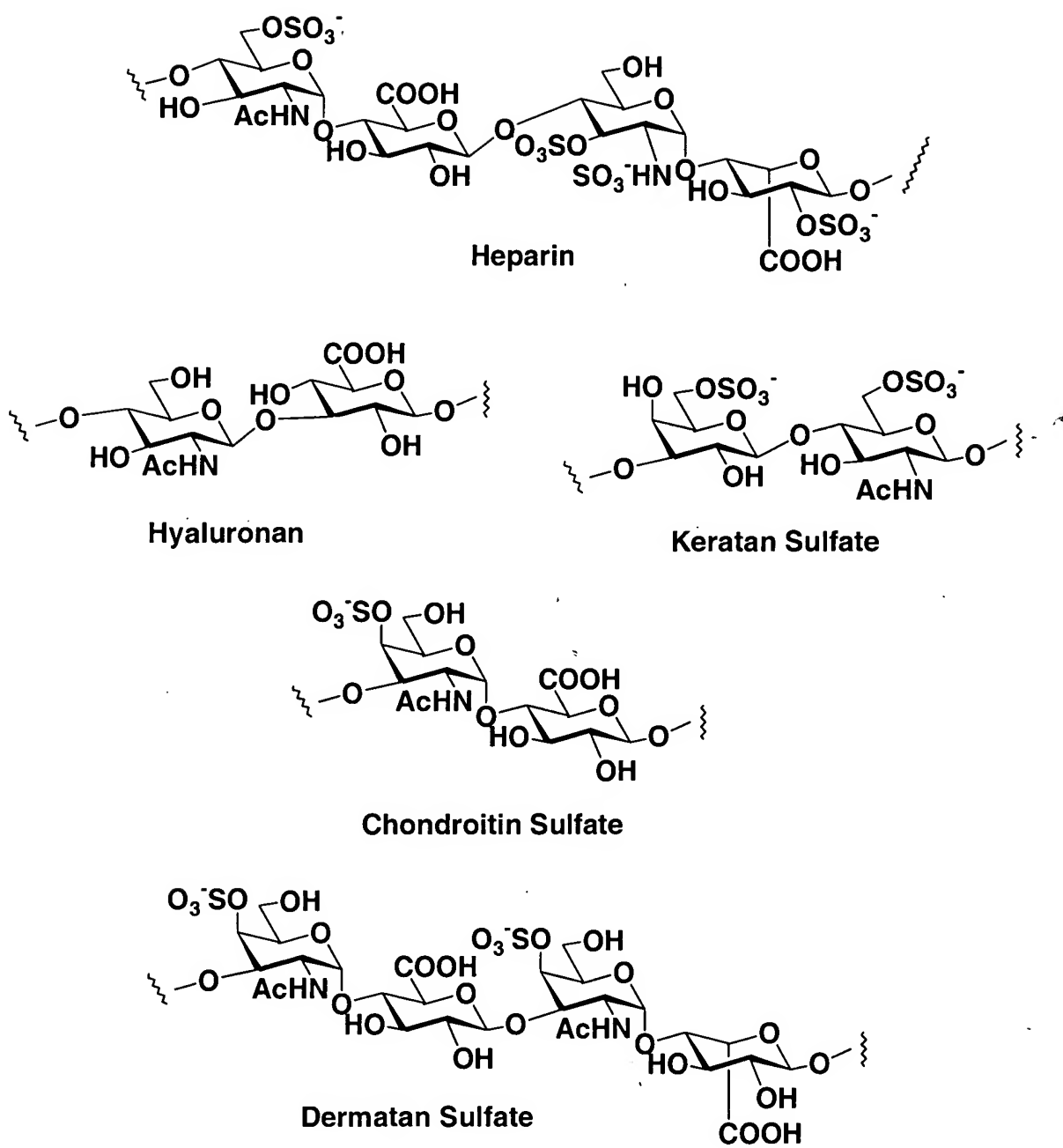
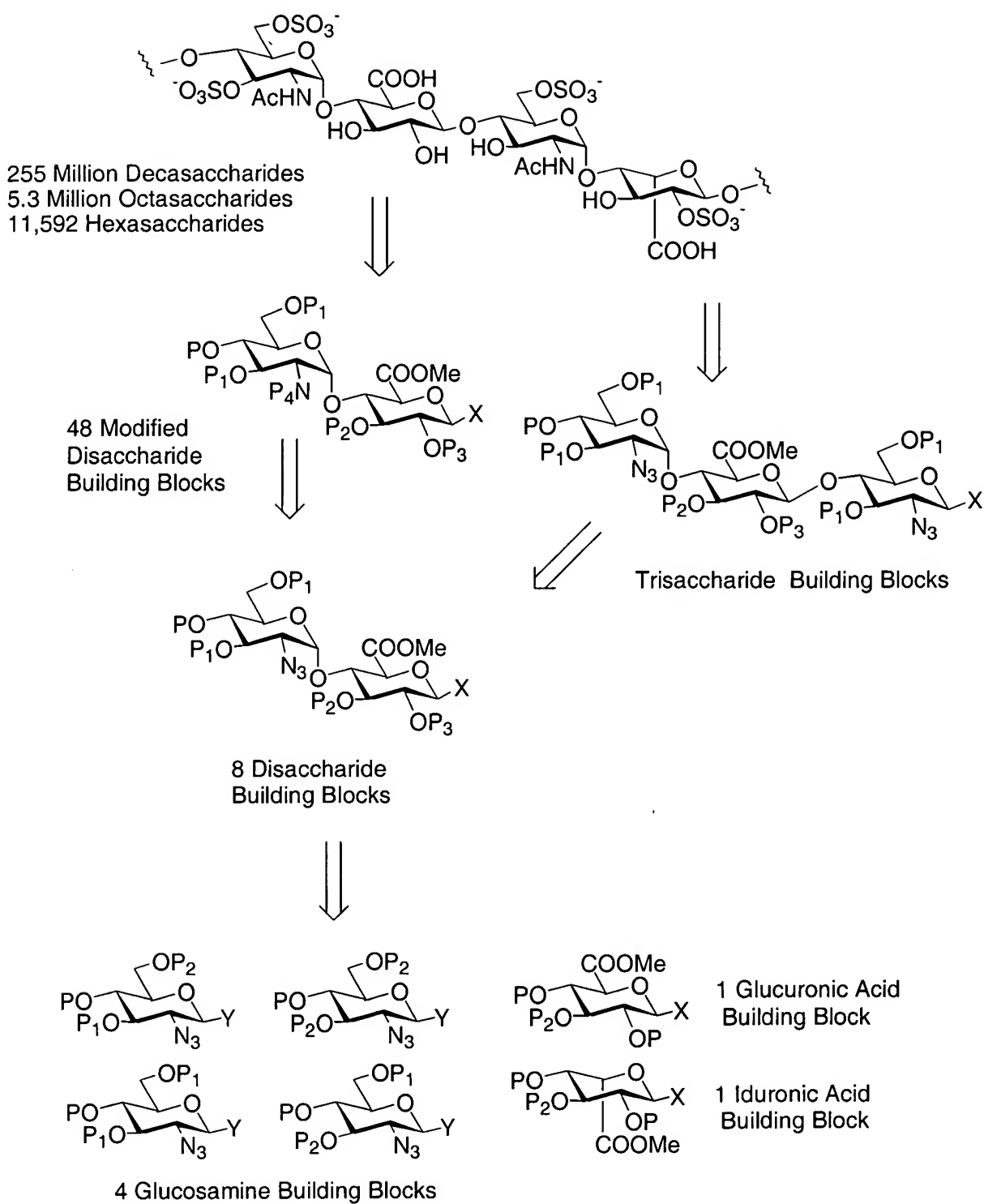


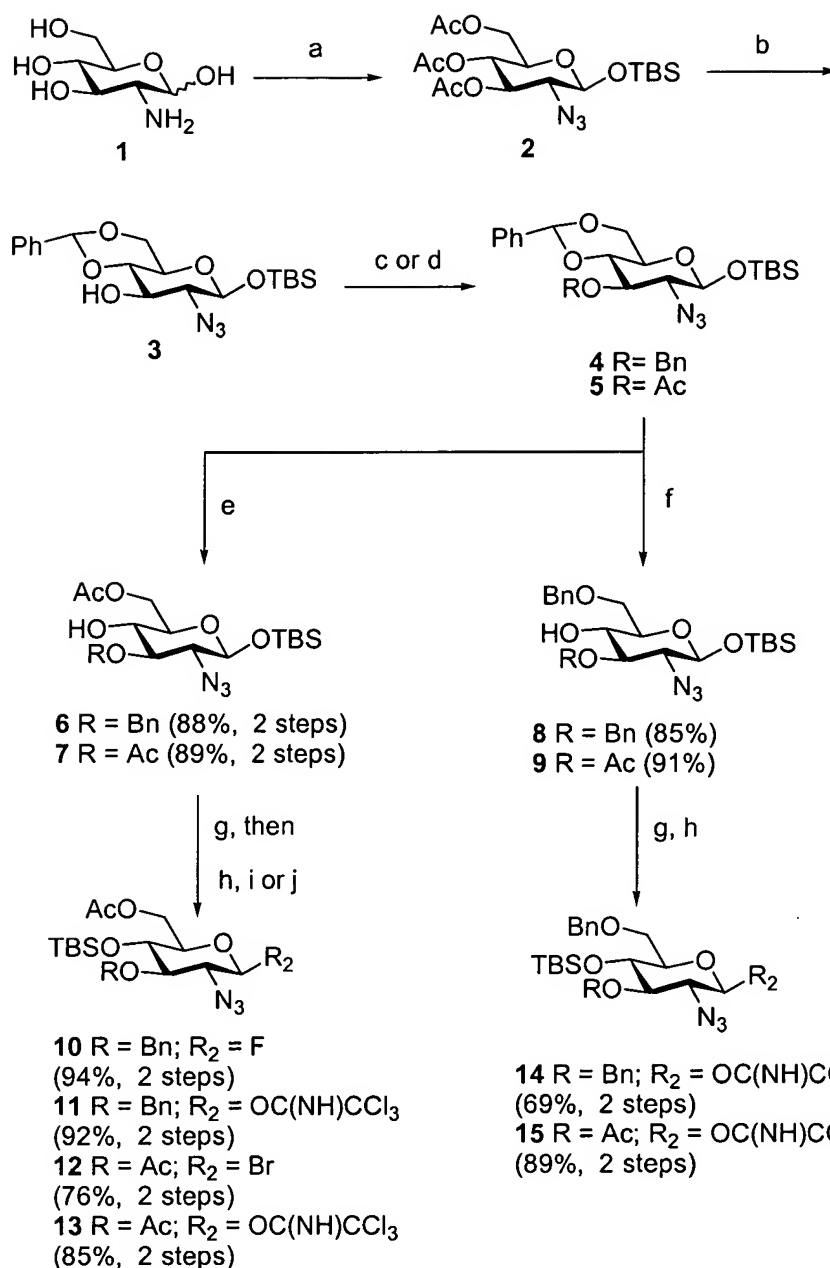
Figure 1



**Figure 2**

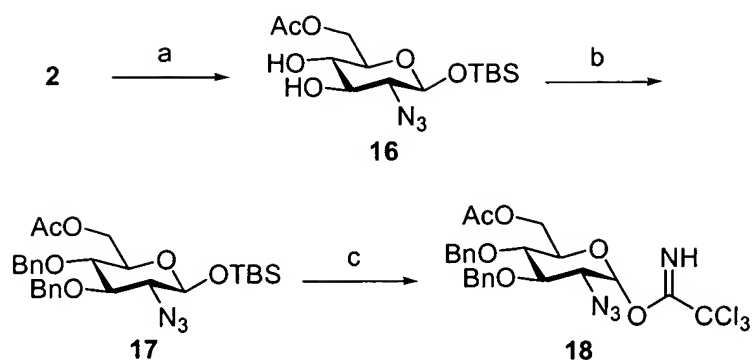


**Figure 3**



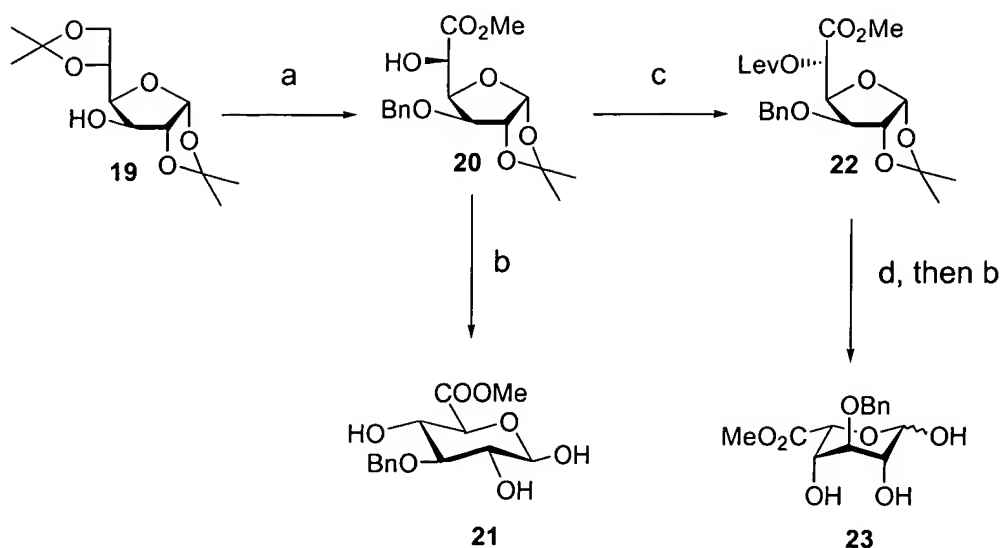
- a) 1. TfN<sub>3</sub>, H<sub>2</sub>O, K<sub>2</sub>CO<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, MeOH, CuSO<sub>4</sub>; 2. Ac<sub>2</sub>O, pyridine, DMAP;  
 3. NH<sub>3</sub>, MeOH, THF; 4. TBSCl, imidazole, CH<sub>2</sub>Cl<sub>2</sub>, 72% (four steps);  
 b) 1. NaOMe, MeOH; 2. PhCH(OMe)<sub>2</sub>, pTsOH, CH<sub>3</sub>CN, 86% (two steps);  
 c) BnBr, Ag<sub>2</sub>O, 4Å molecular sieves, CH<sub>2</sub>Cl<sub>2</sub>, 95%; d) Ac<sub>2</sub>O, DMAP, pyridine;  
 e) 1. TFA (60% aq.), CH<sub>2</sub>Cl<sub>2</sub>; 2. AcCl, collidine, -40°C; f) TES, TFA, CH<sub>2</sub>Cl<sub>2</sub>;  
 g) 1. TBSOTf, lutidine, CH<sub>2</sub>Cl<sub>2</sub>; 2. TBAF, AcOH, THF; h) CCl<sub>3</sub>CN, DBU, CH<sub>2</sub>Cl<sub>2</sub>;  
 i) DAST, CH<sub>2</sub>Cl<sub>2</sub>, 0°C; j) SOBr<sub>2</sub>, imidazole, THF.

**Figure 4**



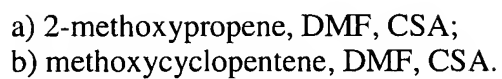
- a) 1. NaOMe, MeOH; 2. AcCl, collidine,  $-40^{\circ}\text{C}$ , 93% (two steps);  
 b) BnBr,  $\text{Ag}_2\text{O}$ , 4Å molecular sieves,  $\text{CH}_2\text{Cl}_2$ , 80%;  
 c) 1. THF, AcOH, TBAF; 2.  $\text{CCl}_3\text{CN}$ , DBU,  $\text{CH}_2\text{Cl}_2$ , 88% (2 steps).

Figure 5



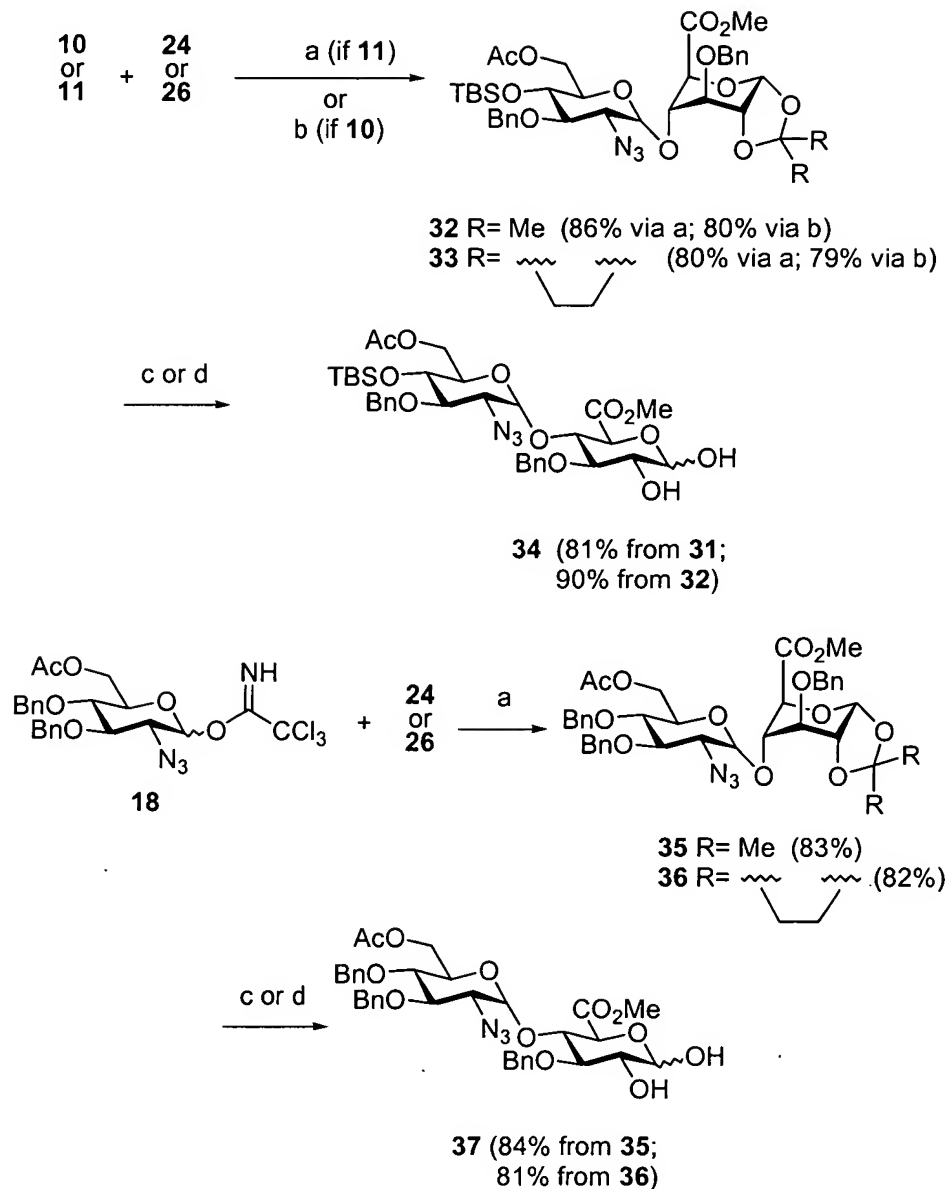
a) 1. NaH, BnBr, THF, Bu<sub>4</sub>NI; 2. aq. HOAc (66%), 40°C; 3. TBSCl, DMAP, CH<sub>2</sub>Cl<sub>2</sub>, pyridine; 4. Ac<sub>2</sub>O, DMAP, pyridine; 5. HF-pyridine, THF; 6. TEMPO (cat.), KBr, Bu<sub>4</sub>NBr, NaHCO<sub>3</sub>, NaOCl, CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O; 7. 4M NaOH, MeOH; 8. MeI, KHCO<sub>3</sub>, DMF, 65% (eight steps); b) TFA (90% aq.), quant; c) 1. Tf<sub>2</sub>O, pyridine, CH<sub>2</sub>Cl<sub>2</sub>; 2. LevONa, DMF, 80°C, 82% (two steps); d) N<sub>2</sub>H<sub>4</sub>, HOAc, pyridine, 91%.

# SECRET



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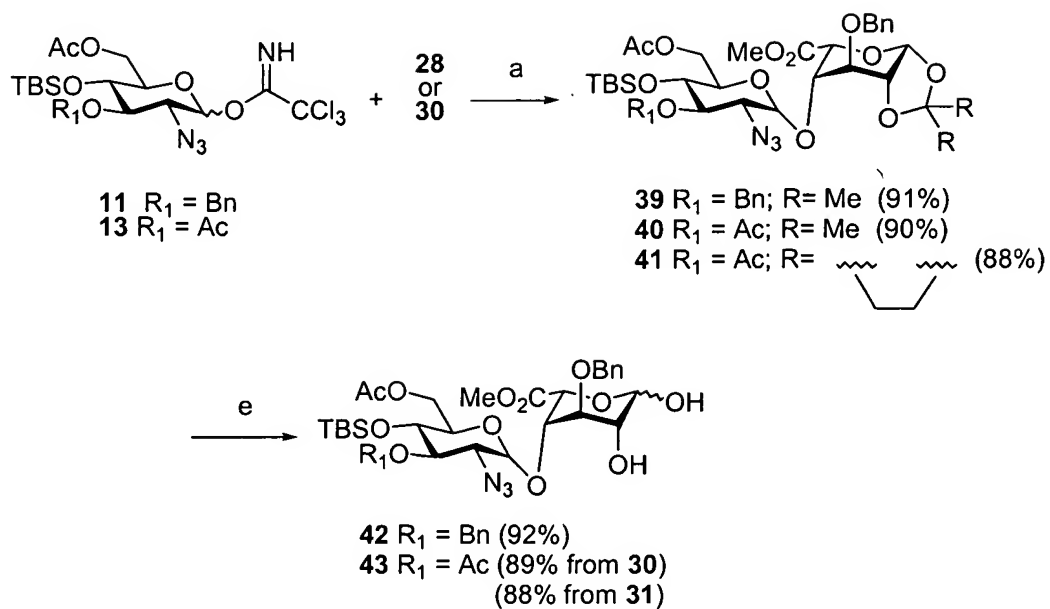
## Glucuronic Acid Acceptors



- a) TBSOTf, 4Å molecular sieves, CH<sub>2</sub>Cl<sub>2</sub>, -78°C to rt;  
b) AgClO<sub>4</sub>, SnCl<sub>2</sub>, Et<sub>2</sub>O, 4Å molecular sieves, 0°C to rt;  
c) dichloroacetic acid (75% aq.);  
d) dichloroacetic acid (50% aq.);  
e) dichloroacetic acid (60% aq.)

**Figure 8**

Iduronic Acid Acceptors

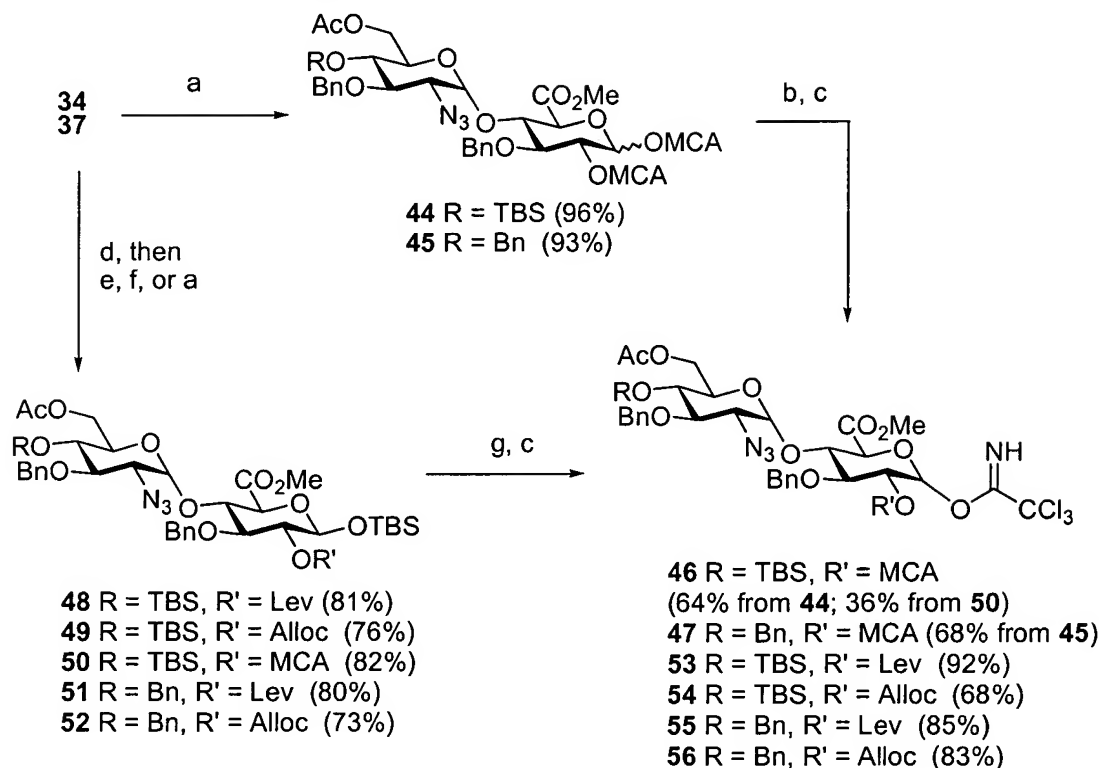


- a) TBSOTf, 4Å molecular sieves,  $\text{CH}_2\text{Cl}_2$ ,  $-78^\circ\text{C}$  to rt;  
 b)  $\text{AgClO}_4$ ,  $\text{SnCl}_2$ ,  $\text{Et}_2\text{O}$ , 4Å molecular sieves,  $0^\circ\text{C}$  to rt;  
 c) dichloroacetic acid (75% aq.);  
 d) dichloroacetic acid (50% aq.);  
 e) dichloroacetic acid (60% aq.)

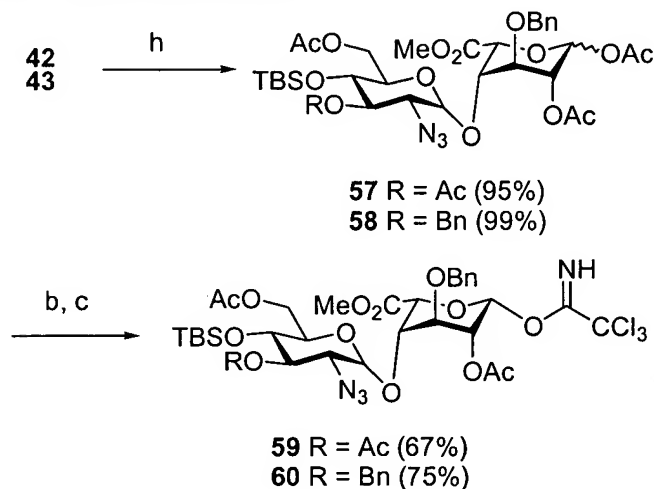


**Figure 9**

**Glucuronic Acid Disaccharide Donors**

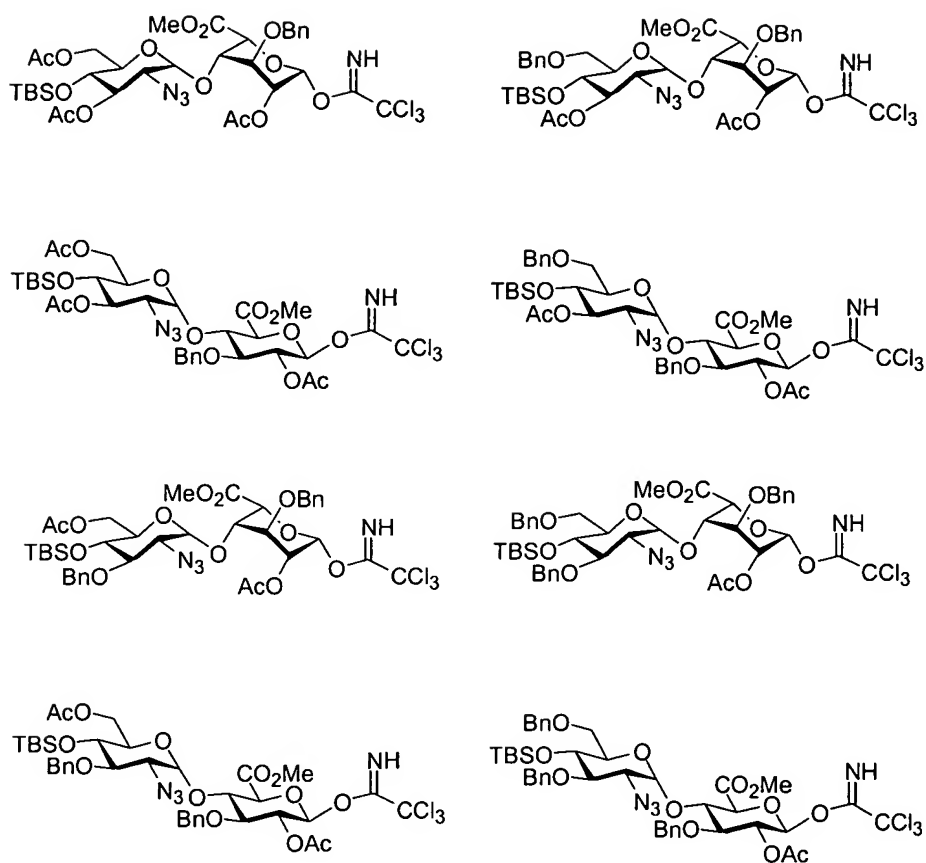


**Iduronic Acid Disaccharide Donors**

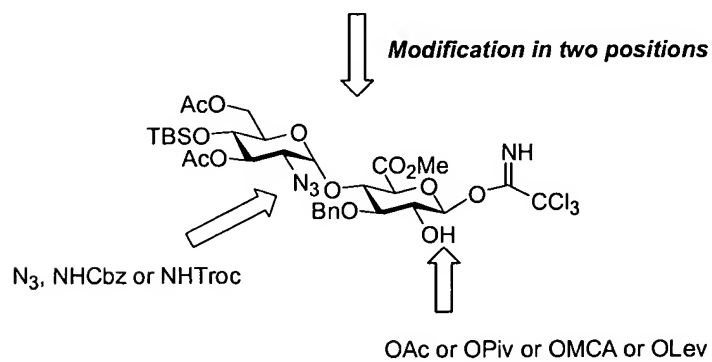


- a) (MCA)<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub>, DMAP, pyridine; b) BnNH<sub>2</sub>, ether, 0°C;  
 c) NCCCl<sub>3</sub>, DBU, CH<sub>2</sub>Cl<sub>2</sub>; d) TBSCl, imidazole, CH<sub>2</sub>Cl<sub>2</sub>;  
 e) (Lev)<sub>2</sub>O, DMAP, CH<sub>2</sub>Cl<sub>2</sub>; f) AllocCl, DMAP, CH<sub>2</sub>Cl<sub>2</sub>;  
 g) TBAF, HOAc, THF; h) Ac<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub>, DMAP, pyridine.

Figure 10



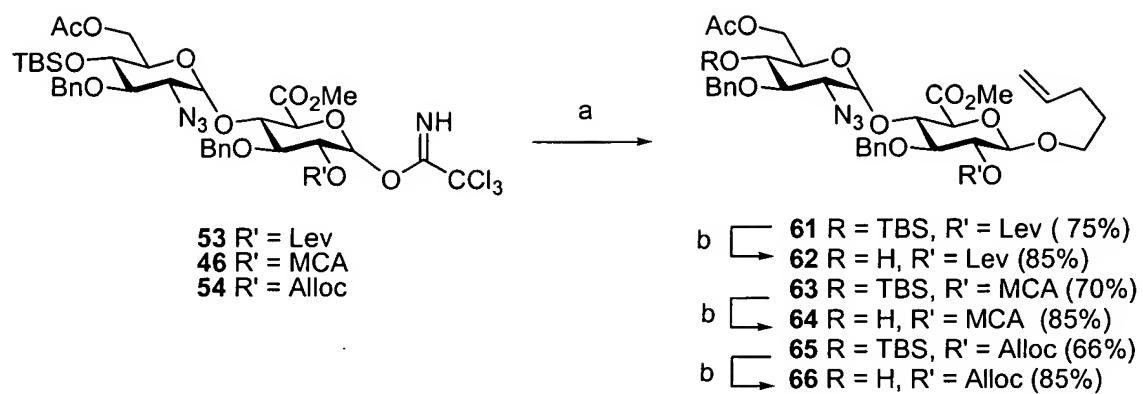
8 Disaccharide Modules



48 Disaccharide Modules

202210-1245007

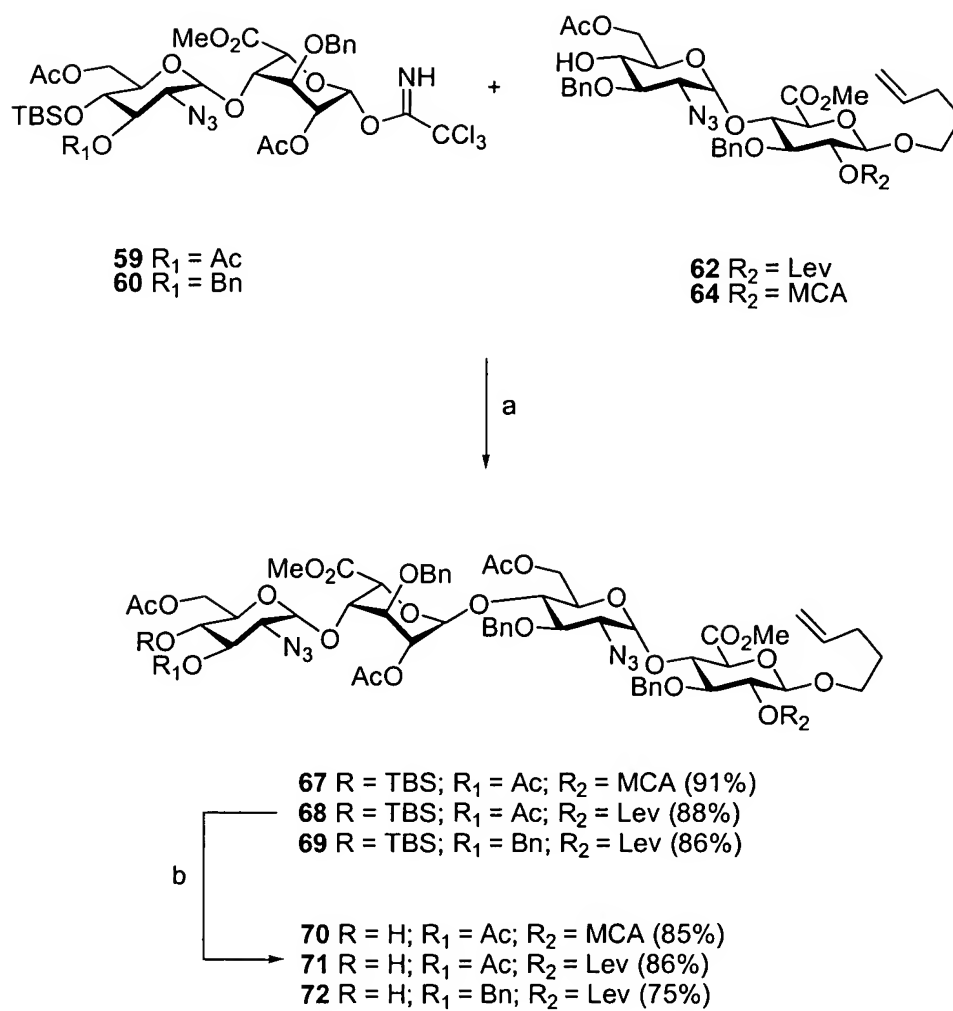
Figure 11



a) 4-penten-1-ol, TMSOTf, CH<sub>2</sub>Cl<sub>2</sub>, 0°C;  
 b) HF-pyridine, HOAc, THF.

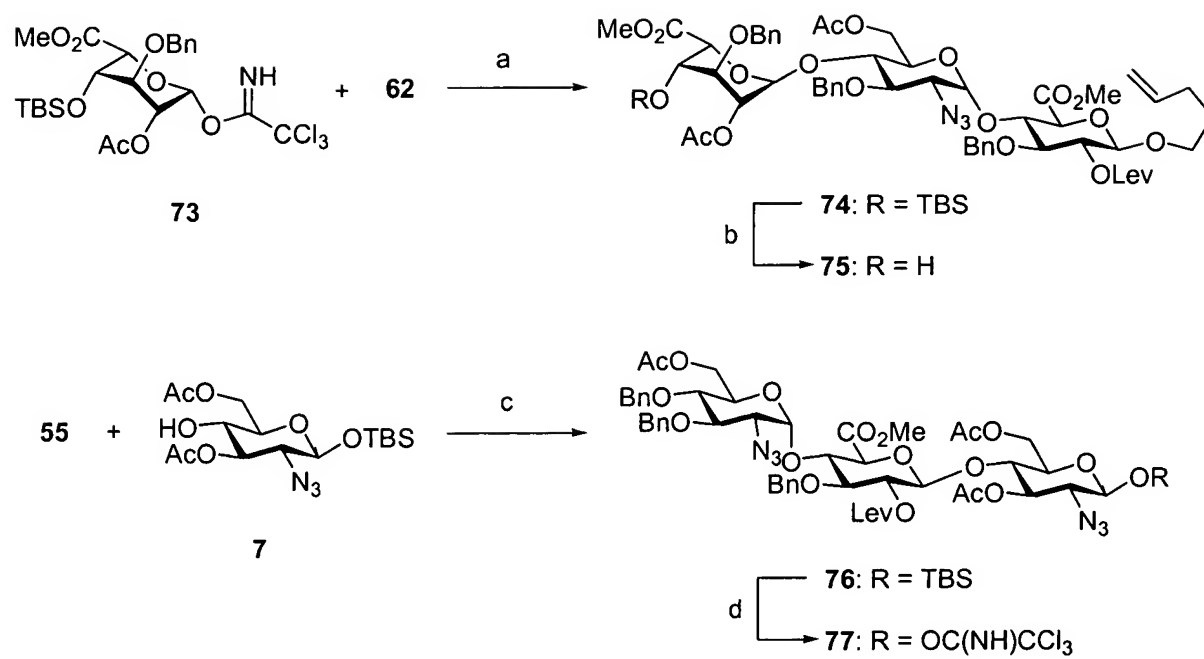
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Figure 12



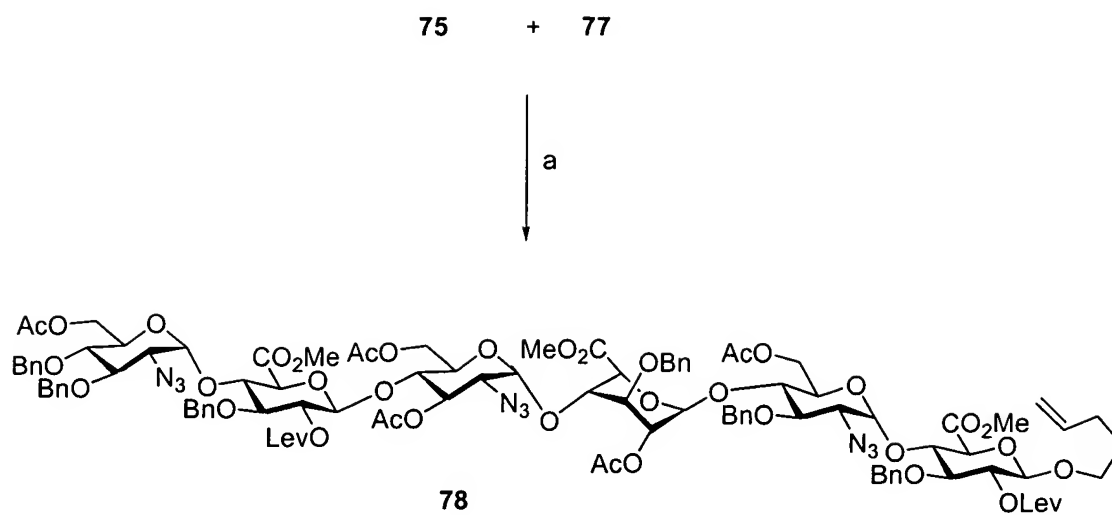
a) TMSOTf,  $\text{CH}_2\text{Cl}_2$ ,  $-20^\circ\text{C}$ ; b) HF-pyridine, AcOH, THF.

Figure 13



a) TMSOTf,  $\text{CH}_2\text{Cl}_2$ ,  $-20^\circ\text{C}$ , 93%; b) HF-pyridine, AcOH, THF, 82%;  
 c) TMSOTf,  $\text{CH}_2\text{Cl}_2$ ,  $-5^\circ\text{C}$ , 63%; d) 1. TBAF, AcOH, THF; 2.  
 $\text{Cl}_3\text{CCN}$ , DBU,  $\text{CH}_2\text{Cl}_2$ ,  $0^\circ\text{C}$ , 87% (2 steps).

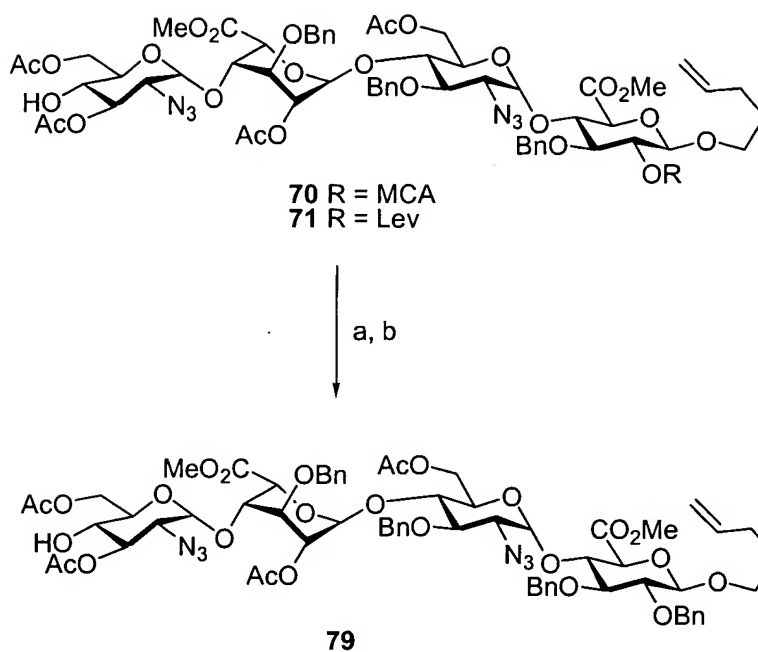
Figure 14



a) TMSOTf, CH<sub>2</sub>Cl<sub>2</sub>, -20°C, 62%;

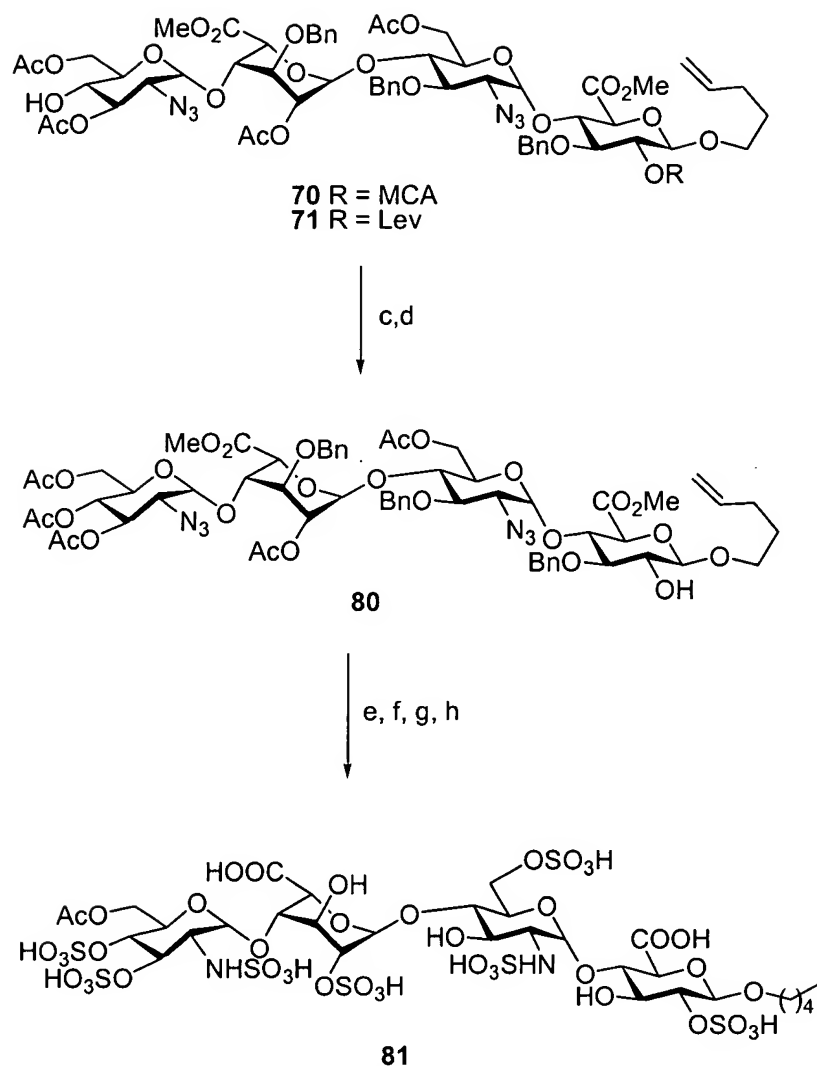
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Figure 15



a) Thiourea, DMF, pyridine, rt, 24 h (90%) b) BnBr, Ag<sub>2</sub>O, 4Å molecular sieves, CH<sub>2</sub>Cl<sub>2</sub>, rt, overnight (76%); c) Ac<sub>2</sub>O, pyridine (quant.); d) NH<sub>2</sub>NH<sub>2</sub>-H<sub>2</sub>O, pyridine, AcOH (90%); e) 1. aq. LiOH (0.7 M), H<sub>2</sub>O<sub>2</sub> (50% aq.), THF overnight; 2. 4 M NaOH, rt overnight (82%); f) Et<sub>3</sub>NSO<sub>3</sub>, DMF, 50°C, overnight (50%); g) H<sub>2</sub>, Pd/C, EtOH, water (quantitative); h) PySO<sub>3</sub>, water (60%).

Figure 16



a) Thiourea, DMF, pyridine, rt, 24 h (90%) b) BnBr, Ag<sub>2</sub>O, 4Å molecular sieves, CH<sub>2</sub>Cl<sub>2</sub>, rt, overnight (76%); c) Ac<sub>2</sub>O, pyridine (quant.); d) NH<sub>2</sub>NH<sub>2</sub>-H<sub>2</sub>O, pyridine, AcOH (90%); e) 1. aq. LiOH (0.7 M), H<sub>2</sub>O<sub>2</sub> (50% aq.), THF overnight; 2. 4 M NaOH, rt overnight (82%); f) Et<sub>3</sub>NSO<sub>3</sub>, DMF, 50°C, overnight (50%); g) H<sub>2</sub>, Pd/C, EtOH, water (quantitative); h) PySO<sub>3</sub>, water (60%).



Figure 17

